

REPORT DOCUMENTATION PAGEForm Approved
OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing this collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden to Department of Defense, Washington Headquarters Services, Directorate for Information Operations and Reports (0704-0188), 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number. PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.

1. REPORT DATE (DD-MM-YYYY) 3 February 2003		2. REPORT TYPE Technical Paper		3. DATES COVERED (From - To)	
4. TITLE AND SUBTITLE Low Melting Salts				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S) ¹ Greg Drake, Tommy Hawkins, Adam Brand, Milton McKay, Leslie Hall ² Keri Tollison, Ashwani Vij, Ismail Ismail, Greg Warmoth, Sarah Sabowski				5d. PROJECT NUMBER 2303	
				5e. TASK NUMBER M2C8	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) ¹ Air Force Research Laboratory (AFMC) AFRL/PRSP 10 East Saturn Blvd. Edwards AFB, CA 93524-7680 ² ERC 10 E. Saturn Blvd. Edwards AFB, CA 93524-7680				8. PERFORMING ORGANIZATION REPORT NUMBER AFRL-PR-ED-TP-2003-033	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) Air Force Research Laboratory (AFMC) AFRL/PRS 5 Pollux Drive Edwards AFB CA 93524-7048				10. SPONSOR/MONITOR'S ACRONYM(S)	
				11. SPONSOR/MONITOR'S NUMBER(S) AFRL-PR-ED-TP-2003-033	
12. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release; distribution unlimited.					
13. SUPPLEMENTARY NOTES					
14. ABSTRACT <div style="text-align: right; font-size: 2em; font-weight: bold;">20030320 044</div>					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON Sheila Benner
a. REPORT Unclassified	b. ABSTRACT Unclassified	c. THIS PAGE Unclassified	A		19b. TELEPHONE NUMBER (include area code) (661) 275-5693

FILE

DTB

MEMORANDUM FOR PRS (In-House/Contractor Publication)

FROM: PROI (STINFO)

10 Feb 2003

SUBJECT: Authorization for Release of Technical Information, Control Number: **AFRL-PR-ED-TP-2003-033**
✓ Greg Drake (AFRL/PRSP); Tommy Hawkins (AFRL/PRSP); Kerri Tollison (ERC), et al., "Low Melting Salts"

2003 JANNAF PDCS Meeting
(Charlottesville, VA, 22-27 Mar 2003) (Deadline: 03 Mar 2003)

(Statement A)

Low Melting Salts

Greg Drake, Tommy Hawkins, Kerri Tollison[#], Adam Brand, Milton McKay, Leslie Hall,
Ashwani Vij[#], Ismail Ismail[#], Greg Warmoth[#], Sarah Sabowski[#]

AFRL/PRSP and [#]ERC, Inc.
10 East Saturn Boulevard
Air Force Research Laboratory
Edwards Air Force Base, CA 93524-7680

Summary: The synthesis and characterization of several new families of low melting salts was carried out. 4-amino-1,2,4-triazole was alkylated in the N(1) position of the 1,2,4-triazole ring, resulting in 1-R-4-amino-1,2,4-triazolium salts, where R= methyl, ethyl, propyl, isopropyl, butyl, methylcyclopropyl, allyl, and 2-ethanol. These starting salts were metathesized with silver salts of nitrate, perchlorate, and nitrocyanamide making large families of new salts with low melting points and high decomposition onset temperatures.

Introduction

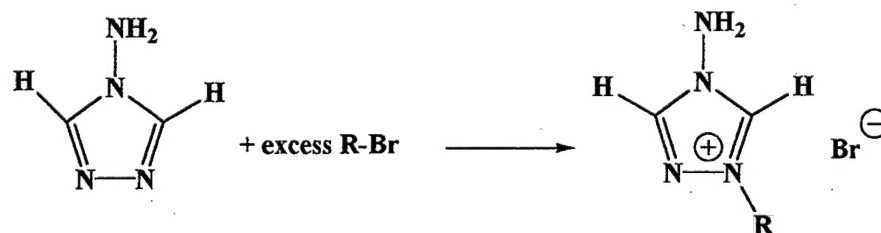
Research in the use of low melting salts based on alkyl 1,3-N, N'-substituted imidazolium cations has increased almost exponentially in the last five years.¹⁻³ Scientists have used them as novel solvents in a wide array of organic synthesis⁴⁻⁶, catalytic work^{7, 8} and separations⁹. Low melting salts offer several inherent advantages over neutral materials, including negligible vapor pressure, wide liquid ranges, and unique solvating power. The physical properties of the ionic liquid can be tailored by judicious choice of the pendant alkyl side chains of the substituted imidazolium cation ring as well as by the nature of the paired anion. However, di-alkyl substituted imidazolium rings suffer from being fuel rich, having relatively poor heats of formation, and low densities.

At AFRL, we have been investigating low melting salts for several years and have discovered similar physical properties with a different, more desirable, parent heterocyclic ring system, 4-amino-1,2,4-triazole. This heterocycle has a high positive heat of formation, significantly higher density, and less fuel content than that of the five-membered, two nitrogen atom imidazole ring. The chemistry used herein is not novel, it was first described by pharmaceutical workers over a decade ago¹⁰ in the search for

making pure 1-substituted-1,2,4-triazole systems. We have improved and expanded this process to make a large family of new, high purity 1-R-4-amino-1,2,4-triazolium bromide salts in essentially quantitative yields. Subsequent metathesis with the appropriate silver salts led to several new families of nitrate, perchlorate and nitrocyanamide ionic liquids. These materials were characterized by vibrational spectroscopy, multinuclear nmr, elemental analyses, DSC studies, and initial impact and friction studies.

General Synthesis and Characterization

Previously, a communication reported the alkylation 4-amino-1,2,4-triazole forming 1-alkyl-4-amino-1,2,4-triazolium salts with subsequent diazotization of the N-amino group to form desired 1-substituted-1,2,4-triazoles.¹⁰ However, the intermediates were not focused upon since the real effort was at the pharmaceutically active 1-substituted-1,2,4-triazoles.^{11,12} We realized that the intermediate salt materials have a similar shape to the well known class of ionic liquids based upon 1,3 di-substituted imidazolium cations. These new materials would make a highly desirable family of precursor halide salts that could open the door to many new families of energetic salts. We improved the reaction scheme by increasing the mole ratio of alkyl halide to greater than 2:1 mole ratio to 4-amino-1,2,4-triazole, which was much greater than the 1:1 or 1:1 mole ratio previously reported, and this also facilitated better precipitation of the product salts from the reaction solution. A large family of new 1-substituted-4-amino-1,2,4-triazolium cations have been synthesized and fully characterized. The synthesis of all of the materials was accomplished by the reaction of excess n-bromoalkane with 4-amino-1,2,4-triazole (< 2:1 mole ratio) in acetonitrile. The product salts precipitated from the reaction mixture upon cooling. (Reaction 1)



Reaction 1. The reaction of 4-amino-1,2,4-triazole with excess alkyl halide to form the desired 1-R-substituted-4-amino-1,2,4-triazolium bromide.

Most of the materials precipitated as oils initially but could be induced to solidify by complete removal of the solvent, followed by recrystallization from hot acetonitrile or isopropyl alcohol. Alkyl side chains including methyl, ethyl, n-propyl, isopropyl, n-butyl, methylcyclopropyl, 2-propenyl(allyl), 2-hydroxyethyl were synthesized via this reaction pathway. The two fold symmetry of the 4-amino-1,2,4-triazole ring was broken by substitution in the one position of the triazole ring, resulting in the emergence of two separate peaks of equal intensity for both the C(3) and C(5) atoms of the 1,2,4-triazole rings as well as for their attached protons in the ^1H and ^{13}C nmr spectra of the crystalline salts. Similarly, these ^1H and ^{13}C peaks were shifted downfield in their respective spectra as well as a shift downfield of the N-amino NH_2 protons from those observed in the starting, neutral heterocycle. This can be attributed to the loss of electron density via quarternization of N(1) atom of the 1,2,4-triazole ring and the formal +1 charge upon the entire cation as a whole.¹³⁻¹⁸ Typical ^1H and ^{13}C spectra are displayed in Figure 1.

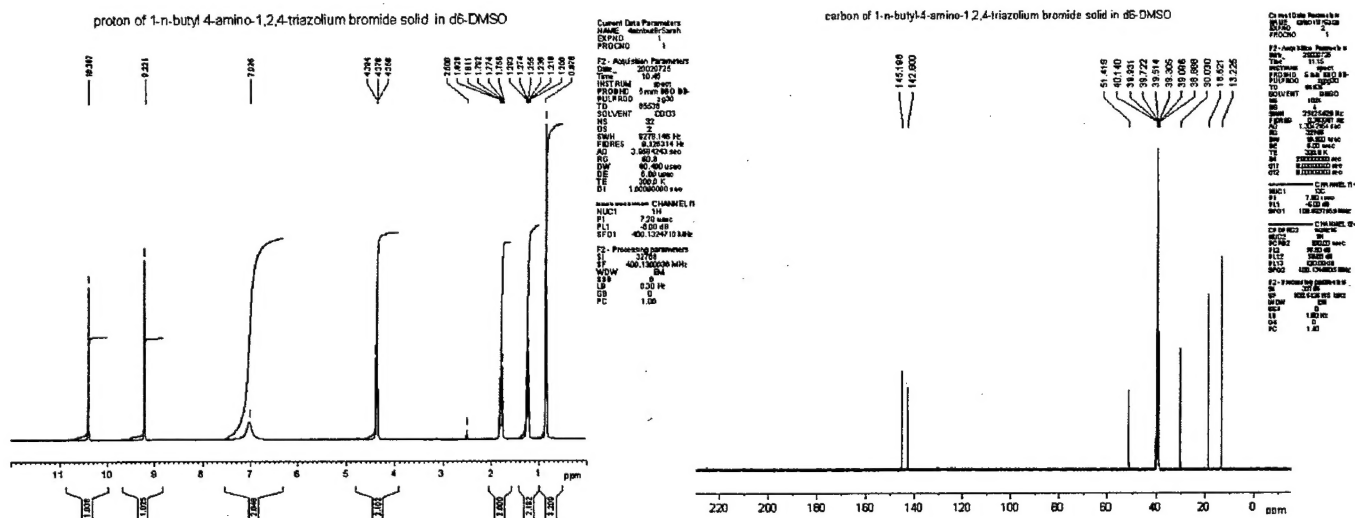


Figure 1. ^1H (left) and ^{13}C (right) of 1-n-butyl-4-amino-1,2,4-triazolium bromide.

Since several of the bromide salts were highly crystalline, single crystal x-ray diffraction studies were carried out on the 1-ethyl-, 1-isopropyl, and 1-methylcyclopropyl substituted 1,2,4-triazolium salts revealing the expected 1-substituted-4-amino-1,2,4-triazolium

cation. In the case of the 1-ethyl- and the 1-methylcyclopropyl- substituted rings, the expected strong hydrogen bond interactions between the N-amino hydrogen atoms of the 4-amino-1,2,4-triazole ring and the bromide anion are observed with close interatomic distances in the crystal lattice. However, in the case of the 1-isopropyl-4-amino-1,2,4-triazolium bromide structure, the bromide anion is sandwiched between the forks of two isopropyl chains of two adjoining 1-isopropyl-4-amino-1,2,4-triazolium cations in the lattice with no significant hydrogen bonding noted. (Figure 2,3,4) This is somewhat surprising and cannot be easily explained. Further crystal structure investigations are ongoing with the rest of the series to see if there are any trends with the expected hydrogen bonding between the N-amino hydrogen atoms and the bromide anion in the crystal lattice.

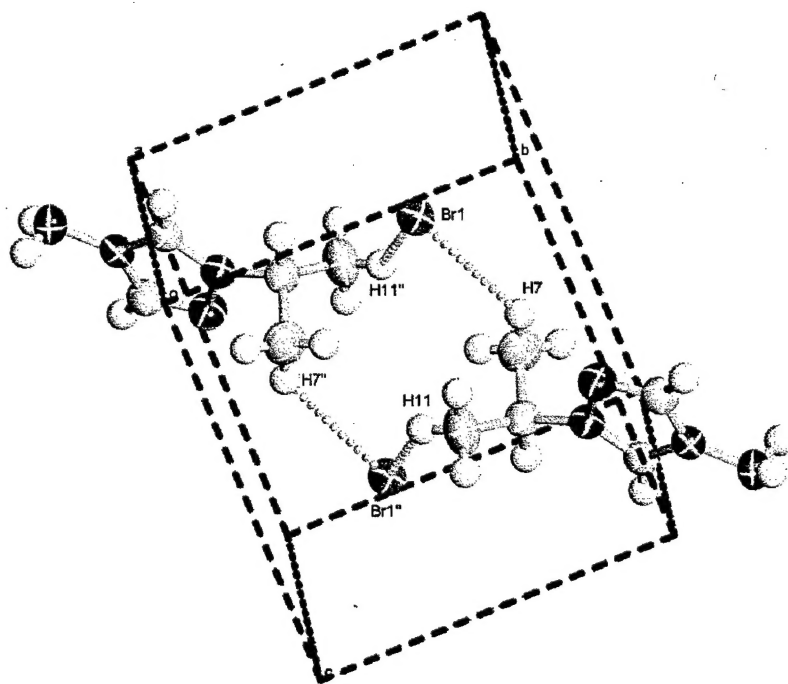


Figure 2. Single crystal x-ray diffraction structure of 1-isopropyl-4-amino-1,2,4-triazolium bromide showing crystal lattice interactions between the cation and the anion.

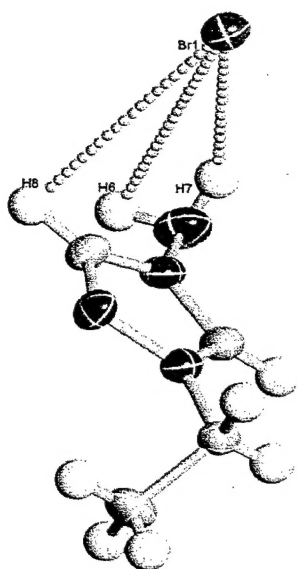


Figure 3. Single crystal x-ray diffraction structure of 1-ethyl-4-amino-1,2,4-triazolium bromide showing crystal lattice interactions between the cation and the anion.

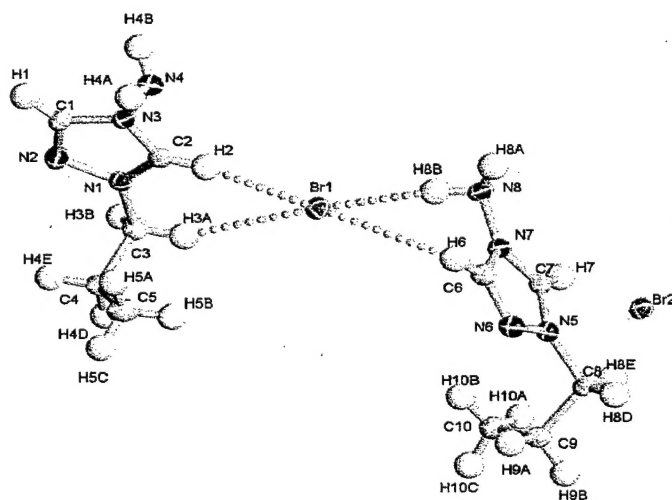
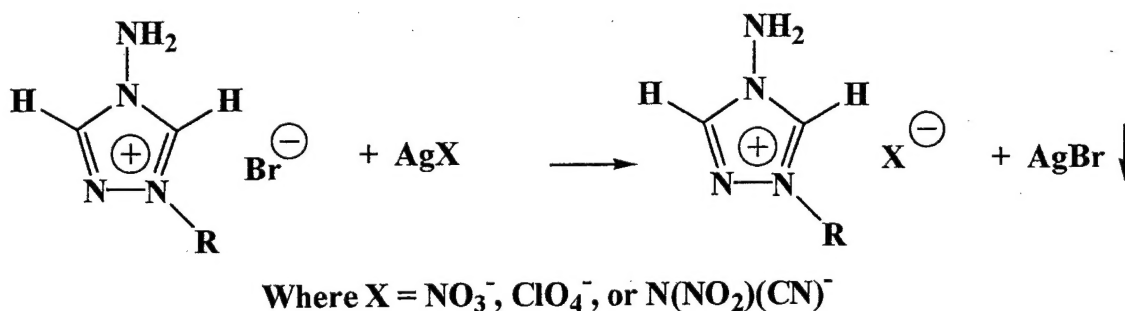


Figure 4. Single crystal x-ray diffraction structure of 1-n-propyl-4-amino-1,2,4-triazolium bromide showing crystal lattice interactions between the cation and the anion.

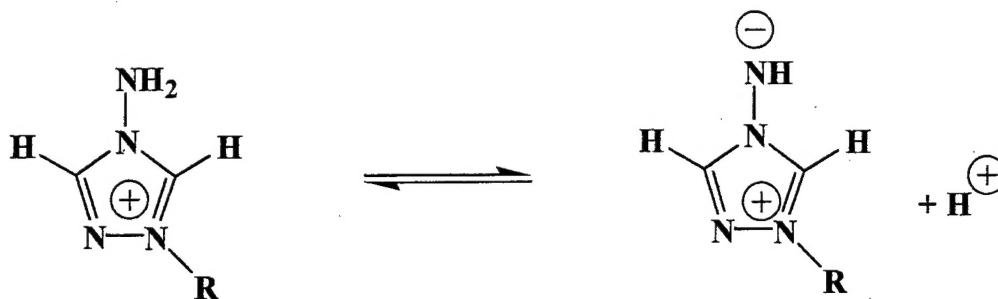
The bromide salts were reacted with either silver nitrate, silver perchlorate, or silver nitrocyanamide in simple metathesis reactions in polar solvents gave clean products after the silver bromide was carefully filtered away. (Reaction 2) Most of the salts were liquids at ambient temperatures, with melting points well below room temperature. All materials were stable at room temperature and showed no signs of decomposition even after over one year of storage at ambient temperatures.



Reaction 2. The metathesis of 1-R-1,2,4-triazolium salts.

Vibrational spectra revealed the presence of hydrogen bonding in the C-H and N-H stretching region (3300- 2900 cm^{-1}) making absolute interpretations difficult. The corresponding energetic anions of the salts (nitrate^{19,20}, perchlorate²¹, and nitrocyanamide²²) were easily identified by their characteristic "fingerprint" bands in their respective infrared and Raman spectra. Despite repeated efforts at crystallization in several polar solvents, either by chilling extremely concentrated solutions or layering of concentrated, highly polar solutions with solvents such as diethyl ether, no reasonable crystals of the any of the energetic salts have been obtained for single crystal x-ray diffraction studies.

As expected all of the 1-substituted-4-amino-1,2,4-triazolium salts are weakly acidic via the equilibrium of the loss of a N-amino NH_2 proton forming a zwitterionic species, 1-substituted-4-imido-1,2,4-triazole. (Reaction 3) Typically the pH of aqueous solutions was around 5 for all of the studied materials. Viscosity was temperature dependent with all of the 1-substituted-4-amino-1,2,4-triazolium salts and was also very dependent on the corresponding paired anion. The nitrate salts were the most viscous



Reaction 3. Weak acid equilibrium for 1-alkyl-4-amino-1,2,4-triazolium cation which lies far to the left, pK_a approx. 7.0×10^{-5} .

followed closely by the perchlorate salts, both anions have relatively high symmetry, while the nitrocyanamide salts were the least viscous, and nitrocyanamide is a low symmetry anion. Work in the near future will attempt to measure the absolute viscosity values of the energetic salts, and try to make correlations with chain length as well as cation anion interactions.

Thermal and Initial Safety Studies

Differential Scanning Calorimetry (DSC) studies revealed the high stability of all of the energetic salts. In many of the salts, a definite melt point could not be obtained, and often only a glass transition could be observed. This was noted even after many cooling/warming cycles ($-100\text{ }^{\circ}\text{C}$ to $50\text{ }^{\circ}\text{C}$) in the DSC cell. This behavior has been noted before in many other ionic liquids¹⁻³, and can often be attributed to poor fit between the cation and anion of the salt. Figure 5 demonstrates a typical DSC study representative of the new energetic ionic liquids obtained, illustrating the low melting point as well as the high decomposition temperature onset.

In Tables 1, 2, and 3, the melting (often glassing point), and the decomposition onsets of the new nitrate, perchlorate, and nitrocyanamide salts have been listed respectively. With the relatively high decomposition onsets, all materials had excellent thermal stability losing significantly less than 1% mass loss per day at $75\text{ }^{\circ}\text{C}$.

Sample: 1-PROPYL-4-AT NITRATE
 Size: 1.8000 mg
 Method: greg
 Comment: 10C/min/10ml/minhermetcalpans

DSC

File: C:\...Files from old DSC\4at propyl no3
 Operator: DRAKE
 Run Date: 16-Jan-02 23:04

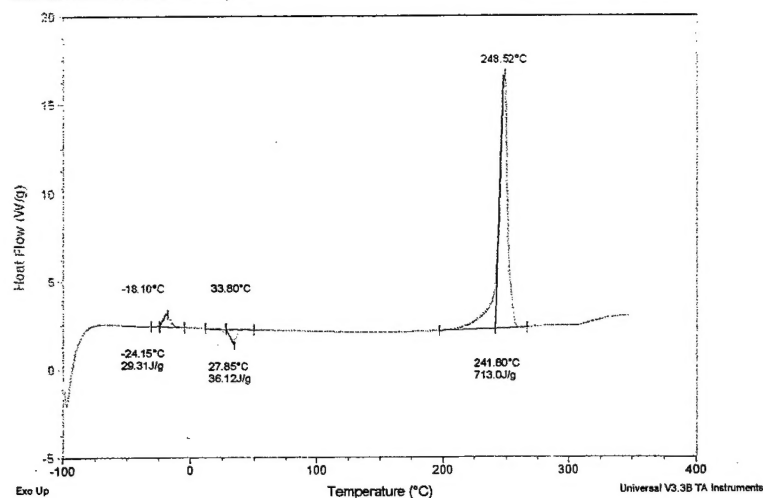


Figure 5. DSC of 1-n-propyl-4-amino-1,2,4-triazolium nitrate.

1-substituted-4-amino-1,2,4-triazolium nitrate salt	Melting point (°C)	Decomposition onset (°C)
1-methyl	54	185
1-ethyl	5	185
1-n-propyl	34	190
1-n-butyl	-10	190
1-ethanol	10	180
1-(2-propenyl)-	10	165
1-methylcyclopropyl	56	190

Table 1. Measured melting/decomposition onset temperatures of the nitrate salts.

1-substituted-4-amino-1,2,4-triazolium perchlorate salt	Melting point (°C)	Decomposition onset (°C)
1-methyl	83	250
1-ethyl	5	195
1-n-propyl	0	190
1-n-butyl	39	240
1-ethanol	10	175
1-(2-propenyl)-	-11	180
1-methylcyclopropyl	5	150

Table 2. Measured melting/decomposition onset temperatures of the perchlorate salts.

1-substituted-4-amino-1,2,4-triazolium nitrocyanamide salt	Melting point (°C)	Decomposition onset (°C)
1-methyl	11	180
1-ethyl	10	175
1-n-propyl	5	185
1-n-butyl	<-10	175
1-ethanol	<-10	175
1-(2-propenyl)-	-10	185
1-methylcyclopropyl	-11	195

Table 3. Measured melting/decomp. onset temperatures of the nitrocyanamide salts.

Some of the salts were tested for their sensitivity to impact and friction. Impact sensitivity was determined on an Olin-Mathieson style drop weight tester. For friction sensitivity, a Julius Peters instrument was employed with ceramic pins and plates. Some general trends were noted and follow the expected nature of the corresponding anion. Most of the nitrate salts are relatively insensitive to impact and friction, the perchlorate salts being significantly more sensitive, while most are still reasonable to work with, and finally the nitrocyanamide salts which were extremely sensitive to impact and friction and should be handled with extreme caution.

Conclusions

Several new families of low melting salts based on 1-alkyl-substituted- 4-amino-1,2,4-triazolium cations were synthesized and well characterized using a variety of techniques. These families of materials all share desirable low melting points yet have relatively high decomposition onsets which make many of these materials interesting for a wide array of uses. Initial safety testing revealed a wide array of relatively insensitive nitrate salts to the highly sensitive nitrocyanamide salts.

Acknowledgements

The authors would like to thank Mr. Mike Huggins (AFRL/PRS), Dr. Ronald Channell (AFRL/PRSP), and Dr. Mike Berman (AFOSR) for financial support as well as for their encouragement and patience for these efforts. One of the authors (S.S.) is indebted for her summer ACS fellowship for outstanding high school scientists. One of the authors (G.D.) would like to thank Dr. Tommy Highsmith (ATKThiokol) and Dr. Jeff Sheehy (Univ. of Alabama at Huntsville/NASA Marshall) for their support, patience, helpful discussions and friendship.

References Cited

1. K.R. Seddon "Room Temperature Ionic Liquids: Neoteric Solvents for Clean Catalysis" Kinetics and Catalysis **1996**, 37, 693.
2. T. Welton "Room Temperature Ionic Liquids. Solvents for Synthesis and Catalysis" Chem. Rev. **1999**, 99, 2071.
3. J. S. Wilkes "A short history of ionic liquids- from molten salts to neoteric solvents" Green Chemistry **2002**, 4, 3.
4. Singer, R. D. ; Hemeon, I. ; Green, L. "1-ethyl-3-methylimidazolium halogenoaluminate ionic liquids as reaction media for the acylative cleavage of ethers" Tett. Lett. **2000**, 41, 1343.
5. Ambler, P. ; Hodgson, P. K. G. ; Stewart, N. J. "Preparation of Butene Polymers using an Ionic Liquid" U.S. Patent # 5,304,615, April 19, **1994**.
6. Abdul-Sada, A. K. ; Atkins, M. P. ; Ellis, B. ; Hodgson, P. K. G. ; Morgan, M. L. M. ; Seddon, K. R. "Alkylation Process" U.S. Patent # 5,994,602, Nov. 30, **1999**.
7. Chauvin, Y. ; Musmann, L. ; Olivier, H. "A Novel Class of Versatile Solvents for Two-Phase Catalysis: Hydrogenation, Isomerization, and Hydroformylation of Alkenes Catalyzed by Rhodium Complexes in Liquid 1,3-Dialkylimidazolium Salts" Angew. Chem. Int. Ed. Engl. **1995**, 34, 2698.
8. Suarez, P. ; Dullius, J. E. L. ; Einloft, S. ; De Souza, R. F. ; Dupont, J. "The use of New Ionic Liquids in Two-Phase Catalytic Hydrogenation Reaction by Rhodium Complexes" Polyhedron **1996**, 15, 1217.

9. Visser, A. ; Swatloski, R. P. ; Rogers, R.D. "Task-specific ionic liquids for the extraction of metal ions from aqueous solutions" Chem. Commun. **2001**, 135.
10. Astleford, B. ; Goe, G.L. ; Keay, J. G. ; Scriven, E. F. V. "Synthesis of 1-alkyl-1,2,4-triazoles: A New One-Pot Regiospecific Procedure" J. Org. Chem. **1989**, *54*, 731.
11. Davis, J. H. ; Forrester, K. J. ; Merrigan, T. "Novel organic ionic liquids(OILs) incorporating cations derived from the antifungal drug miconazole." Tett. Lett. **1998**, *39*, 8955.
12. Dalton, C. R. ; Kane, J. M. ; Kehne, J.H. "3-phenyl-1,4-dialkyl-1,2,4-triazolium Salts and their use antidepressants" U.S. Patent # 5,856,350, January 5, **1999**.
13. Haussen, L. D. ; Baca, E. J. ; Scheiner, P. " Thermodynamics of Proton Ionization from Some Substituted, Unsaturated, Five-Membered Nitrogen Heterocycles (1)" J. Heterocycl. Chem. **1970**, *7*, 991.
14. Claramunt, R. M. ; Sanz, D. ; Catalan, J. ; Fabero, F. ; Garcia, M. A. ; Foces-Foces, C. ; Llamas-Saiz, A. ; Elguero, J. "N-Aminoazoles. Part 2. Basicity and Protonation Site of N-Aminoazoles: an Experimental (pK_a , ^{13}C and ^{15}N NMR Spectroscopy and Crystallography) and Theoretical Study." J. Chem. Soc. Perkin Trans. 2 **1993**, 1687.
15. Lipatova, E. A. ; Shoker, I. N. ; Lopyrev, V. A. ; Pevzner, M. S. "Structure of 3(5) Amino-1,2,4-Triazoles and Their Salts With Inorganic Acids" Khim Geterotsikl. Soedin. Sb. 1. Azotsoderzhashchie Geterotsikly. **1967**, 186.
16. Barlin, G. B. ; Batterham, T. J. "The Proton Magnetic Resonance Spectra of Some Diazoles, Triazoles, and Tetrazoles" J. Chem. Soc. (B). **1967**, 516.
17. Slovetskii, V. I. ; Brusnikina, V. M. ; Khmel'nitskii, L. I. ; Lebedev, O. V. "Special Features of the Structure of Some Salts of Triazole Bases" Khim. Geterotsikl. Soedin. **1966**, *2*, 448
18. Weigert, F. J. ; Roberts, J. D. "Nuclear Magnetic Resonance Spectroscopy. Carbon-13 Spectra of Five-Membered Aromatic Heterocycles" J. Amer. Chem. Soc. **1968**, *90*, 3543.
19. Nakagawa, I. ; Walter, J. L. "Optically Active Crystal vibrations of the Alkali-Metal Nitrates" J. Chem. Phys. **1969**, *51*, 1389.

20. Williamson, K. ; Li, P. ; Devlin, J. P. "Vibrational Studies of the nitrate anion" J. Chem. Phys. **1968**, *48*, 3891.
21. Cohn, H. "Infra-red Spectrum of Crystalline Potassium Perchlorate. Reassignment of the Lower Fundamental Frequencies of the Perchlorate Ion." J. Chem. Soc. **1952**, 4282.
22. Drake, G. W.; Hawkins T. W.; Tollison, K. ; Brand, A. ; McKay, M. ; Ismail, I. ; Petrie, M. A.; A. Vij "Synthesis and Characterization of Energetic Nitrocyanamide, $N(NO_2)(CN)^-$ Salts" manuscript in progress, **2003**.